Standard Operating Procedure for the Determination of Pesticides and Polychlorinated Biphenyls in Water by Gas Chromatography with an Electron Capture Detector.

1.   Scope and Application

   1.1   This method is applicable for the determination of certain organophosporous, triazine, organochlorine pesticides and polychlorinated biphenyls (PCB's) in finished drinking water, ground water, and surface waters. The following compounds, although this list is not all encompassing, can be determined using this method:

Analyte	**CAS #**	**Analyte**	**CAS #**
Aldrin	309-00-2	Alachlor	15972-60-8
Atrazine	1912-2429	Butachlor	23184-66-9
BHC-alpha	319-84-6	BHC-beta	319-85-7
BHC-delta	319-86-8	BHC-gamma (Lindane)	58-89-9
Chlordane-alpha	5103-71-9	Chlordane-gamma	5103-74-2
Chloroneb	2675-77-6	Chlorobenzilate	510-15-6
Chlorothalonil	1897-45-6	Chlorpyrifos	2921-88-2
Cyanazine	21725-46-2	4,4'-DDD	72-54-8
4,4'-DDE	72-55-9	4,4'-DDT	50-29-3
Diazinon	333-41-5	Dieldrin	60-57-1
DCPA	709-98-8	Endosulfan I	959-98-8
Endosulfan II	33213-65-9	Endosulfan Sulfate	1031-07-8
Endrin	72-20-8	Endrin Aldehyde	7421-93-4
Endrin Ketone	53494-70-5	Ethalfluralin (Sonolan)	55283-68-6
Etridiazole	2593-15-9	Fenvalerate	51630-58-1
Heptachlor	76-44-8	Heptachlor Epoxide	1024-57-3
Hexachlorobenzene	118-74-1	Hexachlorcyclopentadiene	77-47-4
Malathion	121-75-5	Metolachlor	51218-45-2
Methoxychlor	72-43-5	Metribuzine	21087-64-9
Mirex	2385-85-5	Parathion Ethyl	56-38-2
Parathion Methyl	298-00-0	cis-Permethrin	54774-45-7
trans-Permethrin	51877-74-8	Propachlor	1918-16-7
Propiconazole (Tilt)	60207-90-1	Pendimethalin	40487-42-1
Simazine	122-34-9	trans-Nonachlor	39765-80-5
Triallate (Far-Go)	2303-17-5	Trifluralin (Treflan)	1582-09-8

Multi-Component Analytes	CAS #
Arochlor 1016	12674-11-2
Arochlor 1221	11104-28-2
Arochlor 1232	11141-16-5
Arochlor 1242	53469-21-9
Arochlor 1248	12672-29-6
Arochlor 1254	11097-69-1

Arochlor 1260   11096-82-5
Chlordane (Tech.)
Toxaphene   8001-35-2

1.2   This method is restricted to use by or under the supervision of analysts
       experienced in the use of gas chromatographs (GC) and in the interpretation of
       gas chromatograms. Each analyst must demonstrate the ability to generate
       acceptable results with this method by using the procedure described in the Initial
       Demonstration of Capability.

1.3   Analyte identifications must be confirmed by at least one additional qualitative or
       quantitative technique.

1.4   Analytes that are not separated chromatographically, such as analytes with similar
       retention times, may need different calibration mixtures for quantitation or
       alternate techniques for identification and quantitation.

1.5   Observed detection limits may vary between waters, depending upon the nature of
       interferences in the sample matrix and the specific instrumentation used.

2.   Summary of Method

2.1   A measured volume of sample, approx. 1 L adjusted to a pH 7, is extracted with
       methylene chloride by shaking in a separatory funnel or mechanical tumbling in
       an appropriate bottle and apparatus. Solvent substitution from methylene chloride
       to methyl tert-butyl ether (MTBE) or hexane is performed. The extract is
       concentrated to a volume of 1 ml and analyzed by capillary column gas
       chromatography equipped with an electron capture detector (ECD). GC
       conditions should permit the separation and quantitation of desired analytes.

3.   Definitions

3.1   INTERNAL STANDARD (IS): A pure analyte(s) added to a solution in known
       amount(s) and used to measure the relative responses of other method analytes
       and surrogates that are components of the same solution. The IS must be an
       analyte that is not a sample component.

3.2   SURROGATE ANALYTE (SURR): A pure analyte(s), which is extremely
       unlikely to be found in any sample, and which is added to a sample aliquot in
       known amount(s) before extraction and is measured with the same procedures
       used to measure other sample components. The purpose of a surrogate is to

monitor method performance with each sample.

3.3   LABORATORY DUPLICATES (DUP): Two sample aliquots taken in the analytical lab and analyzed separately with identical procedures. Analysis should give a measure of the precision associated with laboratory procedures, but not with collection, preservation or storage procedures.

3.4   LABORATORY REAGENT BLANK (LRB): An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

3.5   LABORATORY PERFORMANCE CHECK SOLUTION (LPC): A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined method criteria.

3.6   LABORATORY FORTIFIED BLANK (LFB): An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the lab is capable of making accurate and precise measurements at the required method detection limit.

3.7   LABORATORY FORTIFIED SAMPLE MATRIX (LFM): An aliquot of an environmental sample to which known quantities of the method analytes are added in the lab. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8   STOCK STANDARD SOLUTION: A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the lab with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.9   PRIMARY DILUTION STANDARD SOLUTION: A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration and other analyte solutions.

3.10   CALIBRATION STANDARDS (CAL): A solution prepared from the primary

dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.11   QUALITY CONTROL SAMPLE (QCS): A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the lab, and is used to check laboratory performance with externally prepared test materials.

3.12   May: This action, activity or procedural step is neither required nor prohibited.

3.13   May Not: This action, activity or procedural step is prohibited.

3.14   Must: This action, activity or procedural step is required.

3.15   Shall: This action, activity or procedural step is required.

3.16   Should: This action, activity or procedural step is suggested, but not required.

4.   Interferences

4.1   Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

4.1.1   Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent or soaking in detergent water and washing afterwards. Thoroughly rinse with tap and reagent water and let drain dry. Rinse glassware with acetone first, followed by hexane and let drain dry.

4.1.2   After drying, store glassware in a clean environment. To prevent any accumulation of dust or other contaminants, store inverted or capped with aluminum foil.

4.2   Avoid the use of plastics in the laboratory to minimize the interferences from phthalates. Interferences from phthalate esters can pose major problems in pesticide analysis when using an Electron Capture Detector.

4.3   Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe with an appropriate solvent can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of solvent can be made to ensure that accurate values are obtained for the next sample.

4.4   Matrix interferences may be caused by contaminants that are co-extracted from the sample. Clean up of the sample may be required before further analysis or use of an alternate detector may reduce interferences. After analysis of a sample containing high matrix contaminants, one or more injections of solvent can be made to ensure that accurate values are obtained for the next sample.

4.5   It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used for sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected. Also, the use of high purity solvents and reagents will minimize interferences.

5.   Safety

5.1   Each chemical compound or solvent must be treated as a potential health hazard.

5.2   Exposure to these chemicals must be kept to a minimum or reduced to the lowest possible level.

5.3   The laboratory is responsible for training that involves safety procedures, chemical handling and emergency procedures. The laboratory must also keep a current copy of MSDS's for all chemicals involved in the method and other chemicals stored at the laboratory site.

6.0   Equipment and Supplies

        NOTE: Brand names, suppliers and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 pH paper or pH meter

6.2 Glassware

   6.2.1 2 L separatory funnel with TFE-fluorocarbon or ground glass stopcock

   6.2.2 Disposable pipets with pipet bulb

   6.2.3 200 ml Zymark concentration tubes

   6.2.4 Graduated centrifuge tubes

   6.2.5 Graduated cylinders, various volumes

   6.2.6 60 ml dispenser

   6.2.7 Clear or amber auto-sampler vials with caps

   6.2.8 Glass, amber, 4 liter or 1 liter bottles equipped with teflon lined caps

   6.2.9 Volumetric flasks, various volumes

6.3 Eppendorf auto-pipetters or volumetric/graduated pipets of various volumes

6.4 Zymark Turbo-Vap concentrator/evaporator

6.5 Heating mantle capable of constant 30° to 50° C

6.6 Nitrogen gas supply with gas flow controller

6.7 Analytical balance capable of weighing accurately to the nearest 0.0001 gm

6.8 Gas Chromatography Columns: Capillary, packed, multi-capillary or specialized column may be used. The following phases are suitable for pesticide analysis, but this list is not all inclusive of the phases or columns that may be used. Separation of analytes is still dependent upon the column length and diameter, stationary phase properties, oven temperature and the flow of gas through the column.

   6.8.1 100% dimethyl polysiloxane (DB-1, Rtx-1, OV-1)

   6.8.2 5% diphenyl - 95% dimethyl polysiloxane (DB-5, Rtx-5)

6.8.3   35% diphenyl - 65% dimethyl polysiloxane (DB-35, Rtx-35)

6.8.4   50% methyl - 50% phenyl polysiloxane (DB-17, Rtx-50)

6.9   Temperature programmable gas chromatograph suitable for use with a capillary, packed, multi-capillary or specialized column, also equipped with an electron capture detector or other suitable detector. A data system, such as an integrator or electronic chromatography system, should be used to record raw data. System conditions should be optimized for best resolution of peaks and separation of analytes. Conditions will vary depending upon the analytes and columns used for separation.

7.   Reagents and Standards

7.1   Methylene chloride, acetone, hexane, MTBE (pesticide residue quality or equivalent)

7.2   37% Potassium hydroxide solution. (37 grams ACS grade KOH in 100 ml reagent water) CAUTION: Strong base, add KOH to water slowly. Cool solution while stirring. Use adequate eye protection.

7.3   Phosphate Buffer, pH 7 - mix 29.6 ml of 0.1 N HCl and 50 ml of 0.1 M dipotassium phosphate

7.4   Sodium sulfite, ACS grade, granular, anhydrous.

7.5   Reagent water, Pesticide Grade

7.6   Sodium Chloride (NaCl), crystal, ACS grade - Heat treat in shallow tray @ 400° C for a minimum of 4 hrs to remove interfering organic substances. Store in a glass bottle to avoid phthalate contamination.

7.7   Sodium Sulfate (Na_2SO_4), granular, <u>anhydrous</u>, ACS grade.

7.8   The following mixture is to be used as the internal standard: Acenaphthalene-d10, Chrysene-d12 and Phenanthrene-d10. Purchased from Crescent Chemical Company (500ug/mL), Catalog #CC2494.

7.9   The following mixture is to be used as the surrogate standard: 1,3-Dimethyl-2-nitrobenzene, Perylene-d12 and Triphenylphosphate. Purchased from Crescent Chemical Company (500ug/mL), Catolog #CC2495.

7.10   4-Terphenyl-d14 - fortification solution. Purchased from Crescent Chemical
        Company (500ug/mL), Catolog #CC2079A

7.11   Mirex - alternate surrogate standard. Purchased from Crescent Chemical
        Company (100ug/mL), Catolog #7795M.

7.12   Stock Standard Solution - For drink water samples a stock standard solution is
        purchased from Crescent Chemical Company (100 ug/mL), Catolog #CCS376.
        For ground water samples, three customized standard solutions are purchased
        from Protocol Analytical Supplies Inc. (100ug/mL), Catolog #NDDH-ISA-13,
        NDDH-ISB-13 and NDDH-ISC-12.

        7.12.1   Prepare 5 ug/mL intermediate stock standard solution from CCS-376 by
                 accurately pipetting appropriate amount of stock standard into a desired
                 volumetric flask and bring up to volume with MTBE (or suitable solvent).
                 Larger volumes may be used at the convenience of the analyst. If
                 compound purity is certified at 96% or greater, the weight may be used
                 without correction to calculate the concentration of the stock standard.
                 Commercially prepared stock standards may be used at any concentration
                 if they are certified by the manufacturer or by an independent source.

        7.12.2   Store stock standard solutions in glass vials, clear or amber, with TFE-
                 fluorocarbon-sealed screw tops. Store solutions at appropriate
                 temperatures, such as room (ambient) or 4° C.

        7.12.3   Replace Stock Standard Solutions when a problem is indicated.

7.13   Internal Standard Stock Solution - Prepare 100ug/mL intermediate internal
        standard solution by accurately pipetting appropriate amount of internal standard
        stock into a desired volumetric flask and bring up to volume with MTBE (or
        suitable solvent). Store solution in a TFE-fluorocarbon-sealed screw cap bottle
        and store at appropriate temperature.

7.14   Surrogate Standard Stock Solution - Either CCS-2495 mixture or Mirex. can be
        used. The surrogate can be prepared in lab or be commercially prepared, in our
        case, purchased from Crescent Chemical Company at a concentration of 500ug/mL
        and 100ug/mL respectively.

7.15   Laboratory Performance Check Solution - The following solution can also be
        purchased as a commercially prepared check solution. Prepare by accurately
        weighing 0.0010 gm each of chlorothalonil, chlorpyrifos, DCPA and BHC-delta.
        Dissolve each analyte in an appropriate solvent, such as MTBE, and dilute to

volume in individual 10 ml volumetric flasks. Combine 2 ul of the chlorpyrifos stock solution, 50 ul of the DCPA stock solution, 50 ul of the chlorothalonil stock solution and 40 ul of the BHC-Delta stock solution in a 100 ml volumetric flask and dilute to volume. Store in an appropriate container and at a proper temperature. Solution should be replaced when on-going QC indicates a problem.

7.18   GC Degradation Check Solution - The following solution can also be purchased as a commercially prepared check solution. Prepare a solution containing Endrin and 4,4'-DDT each at a concentration of 0.50 ug/ml. This solution will be injected to check for undesirable degradation of these compounds in the injection port by looking for endrin aldehyde and endrin ketone or for 4,4'-DDE and 4,4'-DDD.

8.   Sample Collection, Preservation, and Storage

8.1   Samples are collected in glass, amber, 4 liter or 1 liter bottles equipped with teflon lined caps.

8.2   If residual chlorine is present, 80 mg of sodium sulfite are added per liter of sample. Shake bottle to dissolve sodium sulfite.

8.3   Samples are kept on ice until delivery to lab; then are stored at 4° C.

8.4   Holding time is 14 days for pesticides (except cynazine) and 14 days for PCB's.

8.5   If cyanzine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected fro cyanazine determination MUST NOT be dechlorinated or acidified when collected. However, these samples must be analyzed within 14 days and must be dechlorinated and acidified immediately prior to fortification with the surrogate standard and extraction.

8.5   Extracts are stored at 4° C and away from light. A 14 day maximum extract storage time is recommended. However, analyte stability may be affected by the matrix; therefore, the analyst should verify appropriate extract holding times applicable to the samples under study.

9.   Quality Control

9.1   1 blank, blank spike, matrix spike, and duplicate are required per 10 samples or per set.

9.2   Quality control results are stored in extraction notebook.

9.3   Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. An MDL for each analyte must also be determined.

9.4   Laboratory Reagent Blanks - Before processing any samples the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents changed, a laboratory reagent blank (LRB) must be analyzed. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.5   Initial Demonstration of Capability

   9.5.1   Select a representative fortified concentration, about 10 times the EDL or at a concentration that represents a midpoint of the calibration range for each analyte. Prepare a primary dilution standard in an appropriate solvent containing each analyte at 1000 times the selected concentration. Add 1 ml of the concentrate to each of 4 to 7 1-L aliquots of reagent water, and analyze each of these LFBs according to procedures in section 11.

   9.5.2   For each analyte, the recovery value for all replicates must fall in the range of R +/- 30% using the value for R demonstrated for reagent water in Table 2. The precision of the measurements, calculated as relative standard deviation (RSD), must be 20% or less. For those compounds that fail these criteria, this procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated.

   9.5.3   For each analyte, determine the MDL. Prepare a minimum of 7 LFBs at a low concentration. Estimate a concentration for each analyte that will produce a peak with a 3-5 times signal to noise response. Extract and analyze each replicate according to sections 11 and 12. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day to day variations are reflected in the precision data. Calculate mean recovery and standard deviation for each analyte. Use equation given in section 17 to calculate the MDL.

9.5.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

9.6 The analyst is permitted to modify GC columns, GC conditions, concentration techniques, internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in section 9.5.

9.7 Assessing Surrogate Recovery

9.7.1 When surrogate recovery from a sample or method blank is <70% or >130%, check calculations to locate possible errors, fortifying solutions for degradation, contamination or other obvious abnormalities, and instrument performance. If those steps do not reveal the cause of the problem, re-analyze the extract.

9.7.2 If a LRB extract re-analysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

9.7.3 If sample extract re-analysis meets the surrogate recovery criterion, report only data for the re-analyzed extract. If sample extract re-analysis continues to fail the surrogate recovery criterion, report all data for that sample as suspect.

9.8 Assessing the Internal Standard

9.8.1 When using the internal standard calibration procedure, the analyst must monitor the IS response (peak area or height) of all the samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standards IS by more than 30%.

9.8.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

9.8.2.1 If the re-injected aliquot produces an acceptable internal standard response report the results for that aliquot.

9.8.2.2 If a deviation of greater than 30% is obtained for the re-injected extract, analysis of the sample should be repeated beginning with section 11, provided the sample is still available. Otherwise, report

results obtained from the re-injected extract, but annotate as
suspect.

9.8.3   If consecutive samples fail the IS response acceptance criterion,
immediately analyze a calibration check standard.

9.8.3.1 If the check standard provides a response factor (RF) within 20% of
the predicted value, then follow procedures itemized in section
9.8.2 for each sample failing the IS response criterion.

9.8.3.2 If check standard provides a response factor (RF) which deviates
more than 20% of the predicted value, the analyst must re-calibrate,
as specified in section 10. After calibration is restored, re-analyze
sample extracts that failed section 9.8.2 criteria.

9.9   Assessing Laboratory Performance - Laboratory Fortified Blank

9.9.1   The laboratory must analyze at least one laboratory fortified blank (LFB)
sample with every twenty samples or one per sample set (all samples
extracted within 24 hr period) whichever is greater. The fortified
concentration of each analyte in the LFB should be 10 times the EDL or a
concentration that represents a mid-point of the calibration range. (See
Table 5). Calculate accuracy as percent recovery (X_i). If the recovery of
any analyte falls outside the control limits (see Sect. 9.9.2), that analyte is
judged out of control, and the source of the problem should be identified
and resolved before continuing.

Note: It is suggested that one multi-component analyte (toxaphene,
chlordane or an Arochlor) LFB also be analyzed with each sample set. By
selecting a different multi-component analyte for this LFB each work shift,
LFB data can be obtained for all of these analytes over the course of
several days.

9.9.2   Until sufficient data becomes available from within their own laboratory,
usually a minimum of results from 20 to 30 analyses , the laboratory should
assess laboratory performance against the control limits in Sect 9.5.2 that
are derived from the data in Table 2. When sufficient internal performance
data becomes available, develop control limits from the mean percent
recovery (X) and standard deviation (S) of the percent recovery. These data
are used to establish upper and lower control limits as follows:

Upper Control Limit = $\overline{X} + 3S$

Lower Control Limit = $\overline{X} - 3S$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should not exceed those established in Sect 9.5.2.

9.9.3   It is recommended that the laboratory periodically document and determine its detection limit capabilities for the analytes of interest.

9.9.4   At least quarterly, analyze a QC sample from an outside source.

9.10   Assessing Method Performance - Laboratory Fortified Sample Matrix

9.10.1   The laboratory must add a known concentration to a minimum of 10% of the routine samples or one sample per set, whichever is greater. The added concentration (see Table 5) should not be less than the background concentration of the sample selected for fortification. Ideally, the fortified analyte concentrations should be the same as that used for the LFB (Sect. 9.9). Over time, samples from all routine sample sources should be fortified.

9.10.2   Calculate the percent recovery, P, of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

P = 100 (X-b) / Fortifying concentration,

and compare these values to reagent water recoveries listed in Table 2. The calculated value of P must fall in the range of R $\pm$ 35%. If P exceeds this control limit, and the laboratory performance for that analyte is shown to be in control (Sect. 9.9), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.11   Assessing Instrument System - Laboratory Performance Check (LPC)

9.11.1   Laboratory Performance Check (LPC). After initial demonstration of capability, instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to monitor instrument sensitivity, column performance and

chromatographic performance. Inability to demonstrate acceptable instrument performance indicates the need for re-evaluation of the instrument system. The sensitivity requirements are set based on the EDLs listed in this method (Table 3). If laboratory EDLs differ from those listed in this method, concentrations of the LPC standard components must be adjusted to be compatible with the laboratory EDLs.

9.11.2 Degradation of DDT and Endrin caused by active sites in the injection port and GC columns may occur. This should be checked on a daily basis by injecting the GC degradation check solution. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and the degradation products of Endrin (endrin aldehyde [EA] and endrin ketone [EK]). For 4,4'-DDT, these products will elute just before the parent, and for endrin, the products will elute just after the parent. If degradation of either DDT or Endrin exceeds 20%, re-silanize the injection port liner and/or break off a meter from the front of the column. The degradation check solution is required each day in which analyses are performed.

$$\% \text{ Degrade 4,4'-DDT} = \frac{\text{DDE area} + \text{DDD area}}{\text{DDT area} + \text{DDE area} + \text{DDD area}} \times 100$$

$$\% \text{ Degrade Endrin} = \frac{\text{EA area} + \text{EK area}}{\text{Total Endrin area} + \text{EA area} + \text{EK area}} \times 100$$

Note: If the analyst can verify that 4,4'-DDT, endrin, their breakdown products, and the anlytes in the IPC solution are all resolved, the IPC solution and the GC degradation check solution may be prepared and analyzed as a single solution.

9.12 The laboratory may adopt additional quality control practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples.

10. Calibration

10.1 Establish optimal GC operating conditions for analytes in question. The GC system must be calibrated using an internal or external standard technique. Perform the Endrin and DDT degradation check described in section 9.11. If degradation of either DDT or Endrin exceeds 20%, take corrective action before proceeding with calibration.

10.2 Internal Standard Calibration Procedure - To use this approach, the analyst must select one or more internal standards compatible in analytical behavior to the

compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. A mixture containing Acenaphthene-d10, Chrysene-d12 and Phenanthrene-d10 has been identified as a suitable internal standard.

10.2.1 Prepare calibration standards (see Table 6) at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more of the internal standards, and dilute to volume. The lowest standard should represent analyte concentrations near, but above, their respective EDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together, and calibration standards for toxaphene, chlordane and each of Aroclors must be prepared individually.

10.2.2 Analyze each calibration standard according to the procedure (Sect.11.4). Tabulate response, peak height or area, against concentration for each compound and internal standard. Calculate the response factor (RF) for each analyte and surrogate using the following equation. RF is a unitless value.

$$RF = \frac{(As)(Cis)}{(Ais)(Cs)}$$

where:

As = Response for the analyte measured.
Ais = Response for the internal standard.
Cis = Concentration of the internal standard (ug/L).
Cs = Concentration of the analyte to be measured (ug/L).

NOTE: For options on calculating response factors for multi-component analytes refer to Sect. 12.4.

10.2.3 If the RF value over the working range is constant (20% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (As/Ais) vs. Cs.

10.2.4   The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hrs), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analysis. If the response for any analyte varies from the predicted response by more than $\pm$ 20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Re-analyze sample extracts for those analytes after acceptable calibration is restored. WARNING: A dirty injector insert will cause poor sensitivity for the late eluting analytes.

NOTE: It is suggested that a calibration verification standard of one multi-component analyte also be analyzed each day or per sample set. By alternating the selection of the multi-component analyte chosen, continuing calibration data can be obtained for all of these analytes over a period of several days.

10.2.5   Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from a reference material obtained from an independent source. Results from these must be within the limits used to routinely check calibration (Sect. 10.2.4)

10.3   External Standard Calibration Procedure

10.3.1   Prepare calibration standards as in Sect. 10.2.1, omitting the use of an internal standard.

10.3.2   Starting with the standard of the lowest concentration, analyze each calibration standard according to Sect. 11.4 and tabulate response (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (20% RSD or less), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

NOTE: For options on calculating a calibration factor for multi-component

analytes, refer to section 12.4.

10.3.3 The working calibration curve or calibration factor must be verified on each working day by the procedures described in Sect. 10.2.4. NOTE: It is suggested that a calibration verification standard of one multi-component analyte also be analyzed each day or per sample set. By alternating the selection of the multi-component analyte chosen, continuing calibration data can be obtained for all of these analytes over a period of several days.

10.3.4 Verify calibration standards periodically (at least quarterly) by analyzing a quality control sample from an outside source.

11. Procedure

11.1 Extraction

11.1.1 Mark meniscus of water level in sample container (for later measurement) if 1 liter bottle is used. If 4 liter bottle is used, measure 1 liter into a 2 liter separatory funnel. Add 1 liter of reagent water to appropriate separatory funnels for blanks and blank spikes.

11.1.2 Adjust pH to 7 by adding 50 ml of phosphate buffer. Measure pH with indicator paper or pH meter. Add H_2SO_4 or NaOH if necessary.

11.1.3 Add 100 gm NaCl, seal and shake to dissolve salt.

11.1.4 Add surrogate spike to each sample, add matrix spike and blank spike to each appropriate sample (Table 5).

11.1.5 Add 60 ml of methylene chloride and shake sample for 2 minutes with frequent venting into a fume hood, to release pressure, of the separatory funnel.

11.1.6 Allow organic phase to separate, then collect in 200 ml Zymark tube or round bottom flask for Rotovap, being careful not to allow any water in collection vessel. If an emulsion occurs, employ mechanical techniques to complete the phase separation. Techniques such as centrifuging, gentle rolling of collection vessel, addition of salt and scratching of glass can be used among other possible procedures.

11.1.7 Repeat steps 11.1.5 and 11.1.6 twice more and combine extracts.

11.2   Extract Concentration

11.2.1 Concentrate the methylene chloride extract to approximately 1 to 3 ml in a
Zymark Turbo Vap or round bottom flask for Rotovap. Exchange the
solvents by adding approximately 10 ml of MTBE or hexane. Concentrate
solvent to approximately 1 to 3 ml. Exchange the solvents once more by
adding approximately 10 ml of MTBE or hexane. Concentrate solvent to
approximately 1 to 3 ml.

11.2.2 Transfer contents to a graduated tube using disposable pipets, rinsing
vessel (Zymark or round bottom flask) with MTBE or hexane and
combining liquids.

11.2.3 Evaporate to 1 ml using block evaporator and nitrogen gas, exchanging
twice more using MTBE or hexane.

11.2.4 Bring final volume to 1 ml in graduated tube.

11.2.5 Transfer contents to auto-sampler vial in preparation for GC-ECD analysis.

11.3   Gas Chromatography

11.3.1   Follow the manufacturers "Operating Manual" for proper set-up and
operation of the GC instrument being used. Optimize conditions of the GC
system for analytes in question.

11.3.2 Calibrate the system before each set of samples using a minimum of 3
standards or use one standard to verify system calibration. The standards
and extracts must be in the same solvent, whether it be MTBE or hexane.

11.3.3 If the internal standard calibration procedure is used, add the appropriate
amount of internal standard to each extract prior to injection.

11.3.4 Record resulting peak size in area units.

11.3.5 If the response of the peak exceeds the working range of the system, dilute
the extract and re-analyze on instrument. If internal standard calibration
was used, add an appropriate amount of additional internal standard to
maintain proper concentration.

11.3.6 Refer to the instrument manuals or other manufacturer's manuals on

specific details for trouble-shooting of the gas chromatograph and/or data system when problems arise.

11.4 Identification of Analytes

11.4.1 Identify a sample component by comparison of its retention time to the retention time of components in a standard reference chromatogram. If retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.4.2 Analytes identified by retention time, must fall within a retention time window. The width of window will vary from analyte to analyte based on the interpretation of the standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.4.3 Identification and determining the retention time windows requires expert judgment, especially when components are not resolved chromatographically. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternate techniques, to help confirm peak identification, need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used; e.g., mass spectrometry, or the use of a second chromatography column.

11.4.4 Identify multi-component analytes by comparison of the sample chromatogram to the corresponding calibration standard chromatogram. Identification of multi-component analytes is made by pattern recognition, in which the experience of the analyst is an important factor.

11.4.5 Analytes that are detected must be confirmed on a secondary column or Mass Spectrometer. Confirmation by an alternative detector, or a third confirmation column is highly recommended if possible. It is required if the results of dual column analysis are questionable.

11.4.6 For matrices with many interferences present, sample cleanup procedures are required. If matrix interferences cannot be removed, and alternative detectors cannot be used or are not applicable; detection limits for the affected analytes should be raised to appropriate levels based on the chromatographer's expert judgement for that particular sample.

12.   Calculations and Documentation

12.1   Calculate analyte concentrations in the sample from the response for the analyte using one of the multi-point calibration procedures described in Sect. 10. Do not use the daily calibration verification standard to calculate the amount of method analytes in samples. A chromatography data system, integrator, spreadsheet or a hand held calculator can accomplish this.

12.2   If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the calibration curve or response factor (RF) determined in Sect. 10.2 and the following equation. RF is a unitless value.

$$C(ug/L) = \frac{(As)(Is)}{(Ais)(RF)(Vo)}$$

where:

As = Response for the parameter to be measured.
Ais = Response for the internal standard.
Is   = Amount of internal standard added to each extract (ug).
Vo = Volume of water extracted (L).

12.3   If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 10.3. The concentration (C) in the sample can be calculated from the following equation.

$$C(ug/L) = \frac{(A)(Vt)}{(Vi)(Vs)}$$

where:

A = Amount of material injected (ng).
Vi = Volume of extract injected (uL).
Vt = Volume of total extract (uL).

Vs = Volume of water extracted (ml).

12.4   To quantitate multi-component analytes, use one of the following methods:

Option 1   Calculate an average response factor, calibration factor, or linear regression equation for each multi-component analyte using the combined area of all the component peaks, such as a time window, in each of the calibration standard chromatograms.

Option 2   Calculate an average response factor, calibration factor, or linear regression equation for each multi-component analyte using the combined areas of 3-6 of the most intense and reproducible peaks in each of the calibration standard chromatograms

When quantifying multi-component analytes in samples, the analyst should use caution to include only those peaks from the sample that are attributable to the multi-component analyte. Option 1 should not be used if there are significant interference peaks within the chlordane, Aroclor or toxaphene pattern.

12.5   Standard concentrations should bracket extract concentrations, if extract concentration exceeds the highest standard by more then 20%, dilute extract and rerun. If internal calibration was used, add an appropriate amount of additional internal standard to maintain proper concentration.

12.6   Record analyte results in proper format to be archived. Results are also reported to a Laboratory Information System (LIMS). Report ND (none detected) for specific analytes if results are less than specified detection limits.

12.7   All paper chromatographs, calculations, and results are saved. The results are put in a box labeled by year and month. All results are stored for a minimum of 3 years before they are discarded.

12.8   If an electronic chromatography data system is being used, chromatographs are stored electronically on disks or archived by printing out chromatographs on a printer. The disks are archived along with a notebook describing contents of each specific disk.

13.   Precision and Accuracy

13.1   Reagent water should be used to determine analyte recoveries, MDLs, EDLs and demonstrate method range. In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine

analyte EDLs and demonstrate method range . Analytes were divided into two fortified groups for recovery studies. Analyte EDLs and analyte recoveries and standard deviation about the percent recoveries at one concentration are given in Table 2.

13.2   Synthetic waters should be used to demonstrate applicability of the method to different ground water matrices. In a single laboratory, analyte recoveries from two standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices . Analyte recoveries from the two synthetic matrices are given in Table 2.

14.   Pollution Prevention

14.1   This method uses significant amounts of organic solvents. Try to minimize waste and reuse solvents for other purposes if possible. Recovered solvents should be recycled or properly disposed of.

15.   Waste Management

15.1   It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations.

16.   References

1.   EPA Method 508, Determination of Chlorinated Pesticides in Water by Gas Chromatography with an Electron Capture Detector, Rev 3.1, Edited by J.W. Munch (1995)

2.   Methods for the Determination of Organic Compounds in Drinking Water (EPA/600/R-92/129) August 1992, Method 507.2, 508.3

3.   X-Chrom V2.1, LabSystems (1997)

4.   HP 5890 Series II and HP 5890 Series II PLUS Reference Manual, Manual Part No. 05890-90270, Edition 5, March 1993

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

	Retention Time[a] (minutes)	
	Primary	Alternative
Etridiazole	23.46	22.78
Chlorneb	25.50	26.18
Propachlor	28.90	30.94
Trifluralin	31.62	_[b]
HCH-alpha	31.62	32.98
Hexachlorobenzene	31.96	_[b]
HCH-beta	33.32	40.12
HCH-gamma	33.66	35.36
PCNB (internal standard)	34.00	34.00
HCH-delta	35.02	41.48
Chlorthalonil	35.36	39.78
Heptachlor	37.74	36.72
Aldrin	40.12	38.08
Chlorpyrifos	40.6	_[b]
DCPA	41.14	41.14
Heptachlor Epoxide	42.16	42.16
Chlordane-gamma	43.52	43.86
Endosulfan I	44.20	43.52
Chlordane-alpha	44.54	44.54
4,4'-DDE	45.90	44.88
Dieldrin	45.90	45.90
Endrin	46.92	_[b]
Endosulfan II	47.60	51.68
Chlorobenzilate	47.94	48.28
4,4'-DDD	48.28	46.92
Endrin Aldehyde	48.62	46.92
Endosulfan Sulfate	49.98	49.30
4,4'-DDT	50.32	50.32
Methoxychlor	53.38	53.72
cis-Permethrin	58.48	_[b]
trans-Permethrin	58.82	_[b]
DCB	64.10	_[b]

17. Tables, Diagrams, Flowcharts, Validation Data & Miscellaneous Information

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR
ANALYTES FROM REAGENT WATER AND
SYNTHETIC GROUNDWATERS[a]

Analyte	Fortified Conc. µg/L	Reagent Water		Synthetic Water 1[d]		Synthetic Water 2[e]	
		R[b]	S_r[c]	R	S_R	R	S_R
Aldrin	0.15	86	9.5	100	11.0	69	9.0
Chlordane-alpha	0.15	99	11.9	96	12.5	99	7.9
Chlordane-gamma	0.15	99	11.9	96	12.5	99	6.9
Chlorneb	5.0	97	11.6	95	6.7	75	8.3
Chlorobenzilate	10	108	5.4	98	10.8	102	9.2
Chlorthalonil	0.25	91	8.2	103	10.3	71	9.2
DCPA	0.25	103	12.4	100	13.0	101	6.1
4,4'-DDD	0.25	107	6.4	96	8.6	101	7.1
4,4'-DDE	0.10	99	11.9	96	12.5	99	6.9
4,4'-DDT	0.60	112	16.8	98	11.8	84	8.4
Dieldrin	0.20	87	8.7	103	9.3	82	7.4
Endosulfan I	0.15	87	8.7	102	8.2	84	12.2
Endosulfan Sulfate	0.15	102	15.3	94	1.3	72	9.4
Endrin	0.15	88	8.8	98	9.8	104	9.2
Endrin Aldehyde	0.25	88	7.9	103	11.3	84	6.8
Endosulfan II	0.15	92	10.1	98	10.8	76	3.9
Etridiazole	0.25	103	6.2	91	6.4	98	7.7
HCH-alpha	0.05	92	10.1	106	7.4	86	6.0
HCH-beta	0.10	95	6.7	92	5.5	100	6.2
HCH-delta	0.10	102	11.2	99	11.9	103	7.7
HCH-gamma	0.15	89	9.8	115	6.9	85	7.7
Heptachlor	0.10	98	11.8	85	11.1	85	9.8
Heptachlor Epoxide	0.15	87	8.7	103	7.2	82	4.8
Hexachlorobenzene	0.05	99	21.8	82	9.8	68	6.2
Methoxychlor	0.5	105	13.7	101	10.1	104	9.5
cis-Permethrin	5.0	91	9.1	96	11.5	86	7.1
trans-Permethrin	5.0	111	6.7	97	9.7	102	7.6
Propachlor	5.0	103	9.3	116	4.6	95	9.6
Trifluralin	0.25	103	5.2	86	10.3	87	

[a]Data corrected for amount detected in blank and represent the mean of seven to eight samples.
[b]R = average percent recovery.
[c]S_R = standard deviation of the percent recovery.
[d]Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.
[e]Corrected for amount found in blank; reagent water fortified with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

TABLE 3. SINGLE LABORATORY ACCURACY, PRECISION, METHOD
DETECTION LIMITS (MDLs) AND ESTIMATED DETECTION
LIMITS(EDLs) FOR ANALYTES FROM REAGENT WATER

	Fortified Conc. µg/L	N[a]	Recovery %	RSD %	MDL[b] µg/L	EDL[c] µg/L
Aldrin	0.075	7	66	9	0.014	0.075
Chlordane-alpha	0.015	7	117	8	0.0041	0.0015
Chlordane-gamma	0.015	7	109	3	0.0016	0.0015
Chlorneb	0.50	7	47	34	0.25	0.5
Chlorobenzilate	5.0	8	99	5	2.2	5.0
Chlorothalonil	0.025	7	119	12	0.011	0.025
DCPA	0.025	7	112	4	0.0032	0.025
4,4'-DDD	0.025	7	115	5	0.0044	0.025
4,4'-DDE	0.010	7	127	6	0.0025	0.01
4,4'-DDT	0.060	7	87	23	0.039	0.06
Dieldrin	0.020	7	77	22	0.011	0.02
Endosulfan I	0.015	7	78	25	0.0092	0.015
Endosulfan Sulfate	0.015	7	129	4	0.0024	0.015
Endrin	0.015	7	72	18	0.0062	0.015
Endrin Aldehyde	0.025	7	95	15	0.011	0.025
Endosulfan II	0.015	7	148	35	0.024	0.024
Etridiazole	0.025	7	96	17	0.013	0.025
HCH-alpha	0.025	8	94	8	0.0053	0.025
HCH-beta	0.010	7	95	12	0.0036	0.01
HCH-delta	0.010	7	84	7	0.0020	0.01
HCH-gamma	0.015	7	80	16	0.0060	0.015
Heptachlor	0.010	7	67	7	0.0015	0.01
Heptachlor Epoxide	0.015	7	71	18	0.0059	0.015
Hexachlorobenzene	0.0050	7	115	43	0.0077	0.0077
Methoxychlor	0.050	7	120	11	0.022	0.05
cis-Permethrin	0.50	7	64	24	0.25	0.50
trans-Permethrin	0.50	7	122	9	0.18	0.50
Propachlor	0.50	7	90	18	0.25	0.50
Trifluralin	0.025	7	108	3	0.0026	0.025

[a]N = Number of replicates.
[b]With these data, the method detection limits (MDL) in the tables were calculated using the formula:

$$MDL = S \; t_{(n-1, \; 1-alpha = 0.99)}$$

where: $t_{(n-1, 1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with
n-1 degrees of freedom.
n = number of replicates.
S = standard deviation of replicate analyses.
'EDL = estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136
- Definition and Procedure for the Determination of the Method Detection Limit -
Revision 1.11) or a level of compound in a sample yielding a peak in the final extract
with signal-to-noise ratio of approximately 5, whichever value is higher.

TABLE 4. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc. μg/mL	Requirements
Sensitivity	Chlorpyrifos	0.0020	Detection of analyte; S/N >3
Chromatographic performance	DCPA	0.0500	PGF between 0.80 and 1.15[a]
Column performance	Chlorothalonil	0.0500	Resolution >0.50[b]
	HCH-delta	0.0400	

[a]PGF -- peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where: $W(1/2)$ = the peak width at half height in seconds
$W(1/10)$ = the peak width in seconds at 10th height

[b]Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where: t = the difference in elution times between the two peaks
W = the average peak width, at the baseline, of the two peaks

Table 5. Spiking Concentrations (ng/uL)

Spike appropriate intermediate standard volume to achieve wanted Matrix/Blank Spike concentration. Final volume is 1 ml. [ng/uL => ug/mL=> ug/L]

Component - Protocol Mixture A	Matrix or Blank Spike (ug/mL)	Surrogate Spike (ug/mL)
Aldrin	0.20	
Atrazine	0.20	
BHC - alpha	0.20	
BHC - delta	0.20	
Chlorpyrifos	0.20	
Dieldrin	0.20	
Endosulfan I (alpha)	0.20	
Endosulfan II (beta)	0.20	
Endrin Ketone	0.20	
Metolachlor	0.20	
Propoconazole (Tilt)	0.20	
trans-Nonachlor	0.20	
Tri-allate (Fargo)	0.20	
Component - Protocol Mixture B	Matrix or Blank Spike (ug/mL)	Surrogate Spike (ug/mL)
BHC - beta	0.20	
BHC - gamma (Lindane)	0.20	
Chlordane-alpha	0.20	
Chlorothalonil	0.20	
DDT	0.20	
Diazinon	0.20	
Endrin	0.20	
Fenvalerate	0.20	
Heptachlor	0.20	
Malathion	0.20	
Methoxychlor	0.20	
Methyl Parathion	0.20	
Pendimethalin	0.20	

Component - Protocol Mixture C	Matrix or Blank Spike (ug/mL)	Surrogate Spike (ug/mL)
Alachlor	0.20	
Chlordan-gamma	0.20	
DDD	0.20	
DDE	0.20	
Endosulfan Sulfate	0.20	
Endrin Aldehyde	0.20	
Ethalfluralin	0.20	
Ethyl Parathion	0.20	
Heptachlor Epoxide	0.20	
Metribuzine	0.20	
Simazine	0.20	
Trifluralin	0.20	
Mirex		0.60

Component - Crescent Mixture CCS-376	Matrix or Blank Spike (ug/mL)	Surrogate Spike (ug/mL)
Alachlor	0.20	
Aldrin	0.20	
Atrazine	0.20	
BHC-gamma	0.20	
Bis(2-ethylhexyladipate)	0.20	
Bis(2-ethylhexylphthalate)	0.20	
Butachlor	0.20	
Chlordane-alpha	0.20	
Chlordane-gamma	0.20	
Dieldrin	0.20	
Endrin	0.20	
Heptachlor	0.20	
Heptachlor Epoxide	0.20	
Hexachlorobenzene	0.20	

Hexachlorocyclopentidiene	0.20	
Methoxychlor	0.20	
Metolachlor	0.20	
Metribuzin	0.20	
tranas-Nonachlor	0.20	
Propachlor	0.20	
Simazine	0.20	
Trifluralin	0.20	
1,3-Dimethyl-2-nitrobenzen		0.50
Perylene-d12		0.50
Triphenylphosphate		0.50

Table 6. Typical Calibration Standard Concentrations (ng/uL)*
[ng/uL => ug/ml => ug/L]
[When 1 L sample is extracted and concentrated to 1 ml.]

COMPONENT	Std #1	Std #2	Std #3	Std #4	Std #5
Aldrin	0.025	050	0.10	0.25	0.50
BHC-alpha	0.025	050	0.10	0.25	0.50
BHC-beta	0.025	050	0.10	0.25	0.50
BHC-delta	0.025	050	0.10	0.25	0.50
BHC-gamma (Lindane)	0.025	050	0.10	0.25	0.50
4,4'-DDD	0.025	050	0.10	0.25	0.50
4,4'-DDE	0.025	050	0.10	0.25	0.50
4,4'-DDT	0.025	050	0.10	0.25	0.50
Dieldrin	0.025	050	0.10	0.25	0.50
Endosulfan I (alpha)	0.025	050	0.10	0.25	0.50
Endosulfan II (beta)	0.025	050	0.10	0.25	0.50
Endosulfan Sulfate	0.025	050	0.10	0.25	0.50
Endrin	0.025	050	0.10	0.25	0.50
Endrin Aldehyde	0.025	050	0.10	0.25	0.50
Endrin Ketone	0.025	050	0.10	0.25	0.50
Heptachlor	0.025	050	0.10	0.25	0.50
Heptachlor Epoxide	0.025	050	0.10	0.25	0.50
Methoxychlor	0.025	050	0.10	0.25	0.50
Mirex	0.60	0.60	0.60	0.60	0.60
Cyanazine	0.025	050	0.10	0.25	0.50
Simazine	0.025	050	0.10	0.25	0.50
Fenvalerate	0.025	050	0.10	0.25	0.50
Alachlor	0.025	050	0.10	0.25	0.50
Atrazine	0.025	050	0.10	0.25	0.50
Methyl Parathion	0.025	050	0.10	0.25	0.50
Ethyl Parathion	0.025	050	0.10	0.25	0.50
Metolachlor	0.025	050	0.10	0.25	0.50
Prowl	0.025	050	0.10	0.25	0.50
Triallate	0.025	050	0.10	0.25	0.50
Trifluralin	0.025	050	0.10	0.25	0.50
cis-Chlordane	0.025	050	0.10	0.25	0.50
trans-Chlordane	0.025	050	0.10	0.25	0.50
Ethalfluralin	0.025	050	0.10	0.25	0.50
trans-Nonachlor	0.025	050	0.10	0.25	0.50
Chlorpyrifos	0.025	050	0.10	0.25	0.50
Malathion	0.025	050	0.10	0.25	0.50
Metribuzin	0.025	050	0.10	0.25	0.50
Chlordane Tech.	0.25	0.50	1.00	2.00	5.00
Toxaphene	1.00	2.00	5.00	10.00	20.00
Arochlor (1016,1221,etc)	1.00	2.00	5.00	10.00	20.00

*   The above table does not list all components that can be analyzed by this method. This is just a starting point.
The calibration standards can be adjusted as needed. Each components response to an ECD detector is different,
therefore each low concentration should be verified that it can be seen on that instrument.